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(54) Title: ELECTROCHEMICAL SYNTHESIS OF METAL AND SEMICONDUCTOR NITRIDES (57) Abstract A method by which a metal or semiconductor nitride film or powder can be produced by electrochemical oxidation of the metal or semiconductor in liquid or supercritical ammonia containing an amide salt. The nitride film thickness can be easily controlled by means of the charge passed; the particle size and amount can be easily controlled by the current and charge passed. Control of film stoichiometry is possible by control of the voltage and current at the metal surface. Also disclosed is a pretreatment method for removing an oxide or hydroxide layer from the substrate to be electrochemically oxidised, involving a cyclic voltammetric protocol.		

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ELECTROCHEMICAL SYNTHESIS OF METAL AND
SEMICONDUCTOR NITRIDES

This invention relates to the manufacture of the nitrides of metals and semiconductors. In particular, it
5 relates to the production of nitrides in film or powder form.

Metal nitrides are suitable for a wide variety of applications, ranging from semiconductors to refractory coatings. Many of these applications require the production
10 of a thin film of the nitride on metal. Traditional methods of fabrication of such films involve heating the metal in a stream of ammonia¹ or sputtering or laser desorbing² from the solid nitride at high temperature. The high temperatures and specialised equipment required render such processes
15 expensive, and the high temperature also precludes the formation of layers on heat sensitive samples such as microelectronic devices. Even chemical vapour deposition (CVD) techniques require relatively high substrate temperatures³. Furthermore, control of the stoichiometry of
20 the layer is difficult, and the layers often contain significant amount of contaminant, particularly carbon and oxygen, which adversely affect their physical characteristics.

A particularly useful metal nitride film is titanium
25 nitride, which is used, for example, to coat cutting tools⁴, as a diffusion barrier for microelectronic devices⁵, as a gold coloured surface for jewellery⁶ and as an optical coating⁷. Previous attempts to oxidise titanium in liquid ammonia, with a range of ammonium salts or cyanides as
30 electrolyte, have resulted in the production of mostly gaseous dinitrogen, with small amounts of black and yellow solids which were postulated as being amido-titanium complexes⁸. Other attempts using a similar system resulted in the production of an insoluble titanium-containing solid,
35 which when calcined at high temperatures to yield titanium nitride.

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We have now found that a conducting titanium nitride film can be produced by electrochemical oxidation of titanium metal in liquid ammonia, using an amide salt as background electrolyte. One advantage of using amides is that the high basicity of the resulting solution favours nitride formation. Another advantage over alternative electrolytes is that carbon, oxygen or halogen contamination of the film can be avoided, as none of these species is present in solution.

One practical way of carrying out the method in liquid ammonia is to operate at temperatures at which ammonia is liquid at atmospheric pressure, ie. between approximately -33°C and -78°C. However, it is the state of the ammonia rather than its temperature which is critical, and operation at other temperatures (for example at higher temperatures under elevated pressure) are therefore feasible. The only requirement is that the ammonia be in either a liquid or a supercritical state.

One of the principal commercial applications of the invention will be in the production of titanium nitride. However, further experiments (for example with molybdenum and tungsten) have indicated that the method will be equally applicable to the manufacture of nitrides of many other transition metals (for example zirconium, hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, rhenium, cobalt, rhodium, iridium, iron, ruthenium, osmium, nickel, palladium, scandium, and yttrium, as well as the lanthanides and stable actinides such as uranium) and also of p-block metals such as aluminium, gallium, indium, thallium, tin, lead, antimony and bismuth. The method may also be used for the manufacture of nitrides of semiconductors such as silicon and germanium, and of mixed semiconductors such as gallium arsenide and indium phosphide. Indeed, the invention provides a general method for producing nitrides, the main restriction being simply that the substrate substance must be sufficiently electrically conductive to permit electrochemical oxidation

to occur. Semiconductors doped in conventional fashion may also be used.

The invention therefore provides, in one aspect, a method of producing a nitride film or powder by
5 electrochemical oxidation of a substrate comprising an electrically conductive substance in an electrolyte comprising an amide salt in liquid or supercritical ammonia.

One important factor which will influence nitride formation is the free energy of formation of the nitride at
10 the synthesis temperature and pressure. If this value is negative, then the decomposition of the nitride to form metal (or semiconductor) plus nitrogen is thermodynamically unfavourable. If it is positive, then decomposition is favoured and it may be expected that nitrogen gas will be
15 evolved as a reaction product. It should be remembered that the free energy value is temperature dependent, so that a relatively low temperature synthesis route (such as those which are preferred in methods according to the invention) will tend to decrease the importance of the positive entropy
20 change occurring during the decomposition reaction and make the value of the free energy change more negative, thus favouring nitride formation. The transition metals most suited to nitride formation are those in groups IVa, Va and VIa, namely titanium, zirconium, hafnium, vanadium, niobium,
25 tantalum, chromium, molybdenum and tungsten. However, many of the other transition metals would also be expected to form nitrides with relative ease, for example manganese, iron (and steel), cobalt, nickel, rhenium and uranium. The p-block elements aluminium, gallium, indium, silicon and
30 germanium are a further group of elements who would be expected readily to form nitrides, and other good candidates are the lanthanides and the actinides.

A variety of amides may be used as the background electrolyte, provided that they have a sufficiently ionic
35 nature. Amides of groups IA metals are preferred (ie..

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lithium amide, sodium amide, potassium amide, rubidium amide and caesium amide).

In a preferred method according to the invention, the conducting substrate is subjected to an electrochemical reductive pre-treatment, prior to electrochemical oxidation, in order to remove any surface oxide layer.

The substrate may either be composed wholly or predominantly of the electrically conductive substance, or alternatively the conductive substance may be provided as a surface layer on a substrate of another material which need not itself be conductive. By suitable control of the electrolysis, a nitride film of desired thickness can readily be produced, or alternatively a nitride powder.

The invention is hereinafter described in more detail by way of example only, with reference to various experimental test results and to the accompanying figures, in which:

Figure 1 is a montage of cyclic voltammograms (CVs) obtained at negative potentials for a titanium electrode in a method according to the invention. The voltage sweep rate was 100 mV.s^{-1} and the arrows show the direction of the scan. The starting potential was -0.02V and the initial direction of scan was to more reducing potentials. The cycles shown are (—) 1st cycle, (— —) 2nd cycle (— — —) 3rd cycle and (—) cycle after 30 minutes of cycling.

Figure 2 is a plot illustrating the chronoamperometric transient recorded on the pre-treated titanium electrode. The potential was pulsed to 3V at time zero, then to 4V and subsequently to 5V.

Figure 3 is a montage of Cvs for the oxidation of a titanium electrode with oxide present on its surface. The sweep rate was 20 Mv.s^{-1} , the starting potential was 0V and the initial direction of scan was to more oxidising

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potentials. The cycles shown are (—) 1st scan, (— —) 2nd scan, (- - -) 4th scan.

Figure 4 is a grazing-angle reflectance spectrum of (a) chemically produced titanium nitride (b) a thin film of 5 titanium nitride produced by a method according to the invention, and (c) titanium metal having surface oxide. The y-axis displays the ratio of the intensity of the reflected light to the incident light, in arbitrary units.

Figure 5 is a montage of magnetic susceptibility plots 10 for titanium nitride film produced by a method according to the invention, and for bulk titanium nitride. The measured susceptibilities for the film have been multiplied by a factor of 100 for scaling purposes.

Figure 6 is a montage of the Raman spectra of both film 15 and particles of titanium nitride, produced at high current densities and at room temperature/10 atmospheres by a method according to the invention, together with the Raman spectrum obtained from a commercial sample of titanium nitride.

Figure 7 is a powder X-ray diffraction pattern produced 20 by nano-crystalline titanium nitride powder produced by a method according to the invention.

Figure 8 is a montage of CVs for the electrooxidation of a precleaned molybdenum electrode at a sweep rate of 50mV.s^{-1} . (—) cycle 1 (- - -) cycle 7. The upper limit of 25 the CV was changed with each cycle to steadily more oxidising potentials.

Figure 9 is a plot of the chronoamperometric transient recorded for a pretreated molybdenum electrode at -78°C . The potential was pulsed from 0V to +1.75V at time zero.

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A saturated solution of potassium amide in liquid ammonia at -78°C was prepared by the addition of oxide-free potassium metal (Aldrich) to liquid ammonia (BOC) which had been dried by distillation from sodium metal. The blue colour was discharged by the addition of Fe_3O_4 (Aldrich), which was then removed from the solution, along with the excess potassium amide, by filtration. The electrochemical experiments were performed in 125cm^3 of the solution under dry oxygen-free nitrogen (BOC) using a three electrode system; the working electrode was a piece of titanium foil, of approximate area of one side 1cm^2 (Aldrich), the counter or supporting electrode was a coil of platinum wire (Johnson Matthey) which was of sufficient area to ensure that the current was never limited by the counter electrode reaction, and the reference electrode was a bright platinum wire. All potentials are reported with respect to this reference electrode. A PP2 three-electrode potentiostat (Oxford Electrodes) was used to control the electrochemistry, and the data were recorded on a series 60000 x-y-t chart recorder (Advance Bryans). Glancing-angle specular reflectance measurements on the resulting thin films were recorded using a Spex Fluoromax fluorescence spectrometer under synchronous scan conditions. SQUID (superconducting quantum interference device) measurements were obtained using a Quantum Design instrument. Raman spectra were recorded using a Labram spectrometer (Instruments SA).

In order to remove the protecting layer of surface oxide on titanium metal, a cyclic voltammetric protocol for the titanium working electrode was devised and used. The potential of the electrode was cycled at sweep rates of 50 or 100 mV.s^{-1} between the initial potential (typically around 0V) and a negative potential limit, always well in excess of -1V. The resulting cyclic voltammogram ("CV") is shown in Fig 1. The negative potential limit was chosen in order to produce a large negative current, typically of the order of several mA, in the sweep to negative potentials. This large current is thought to be caused by reduction of solvent, film and/or electrolyte; possible candidates are the

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evolution of hydrogen at the working electrode surface, the reduction of the oxide film, or the deposition of potassium. During the reverse sweep to 0V, an associated oxidation peak can clearly be seen at approximately -1.5V. On continued
5 cycling, this oxidation peak was observed to diminish as the reduction wave shifted to more negative potentials. The CV recorded after 30 minutes showed little reduction in the negative sweep and no oxidation peak in the positive sweep at these potentials. It is likely that these reduction and
10 oxidation reactions are associated with the oxide layer, and therefore that this CV cycling to negative potentials has resulted in the reduction and loss of the oxide layer and the production of a bare titanium electrode. It is believed that this process produces a clean titanium surface, and is
15 preferable to pulsing to anodic potentials⁸, which will merely disrupt the oxide layer whilst not completely removing it.

Fig 2 shows the current time transient obtained on the pre-treated titanium electrode for a chronoamperometric
20 experiment, when its potential was stepped from 0V (no oxidation) to 3V. A large positive current of the order of several mA was initially observed, indicative of oxidation at the electrode surface, which fell slowly with time. Increasing the electrode potential (first to 4V, then to 5V)
25 resulted in an increase in the oxidation current as shown, as did increasing the temperature of the solution from -78°C to -33°C. There was no sign of gaseous nitrogen evolution. Stirring of the stagnant solution did not result in an increased current, which indicates that the current is
30 not limited by the mass transport of solution species to the electrode. These results are consistent with the growth of a surface film on the electrode surface by an oxidation which involves liquid ammonia and/or amide. The electrode was disconnected after 35 minutes, after which time it was
35 a golden colour, indicating the presence of a surface film. The total charge passed in this process would be enough to form a surface layer of a titanium (III) species of several hundred layers' thickness. This is consistent with the

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observation of a gold-coloured layer, indicating that the film is the major oxidation product.

CV studies of the oxidation of a titanium electrode in a liquid ammonia system also indicate the growth of a surface film, as is shown in Fig 3. The first sweep to oxidising potential shows an oxidation current due to nitride film growth. Subsequent cycles result in the progressive shift of this oxidation to more positive potentials. The increase in the potential window accessible by this electrode by more than 1V, coupled with the retention of a similar pseudocapacitance indicates that the deposited film is relatively inert and is conducting; this is a strong indication that the film is titanium nitride. These studies also indicate that complete oxide removal is not an essential prerequisite to film deposition. CV experiments with titanium electrodes which have not had the oxide layer fully removed show similar oxidation characteristics, indicating the growth of a surface nitride film. However, these films would have been deposited onto the oxide layer, and would therefore be expected to suffer from the effects of incorporated oxygen contaminant; also the currents passed in the oxidation for oxide coated films are smaller.

Fig 4 shows the reflectance spectrum obtained for titanium oxide, titanium nitride produced chemically and the titanium nitride film produced in the chronoamperometric experiment detailed above. It is clear that the electrochemically produced film shows increased reflectivity in the ultra-violet region of the spectrum (below 300 nm) compared with titanium oxide. Furthermore, the measured reflectance spectrum of the chemically produced titanium nitride film is extremely similar to that of the electrochemical film, indicating that the electrodeposited film is indeed titanium nitride.

This film has been further characterised by SQUID measurements. Titanium nitride shows a characteristic

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transition from metallic to superconducting behaviour in the range $<1.17 - 5.8\text{K}^{(10)}$. Thin films of titanium nitride would be expected to show a similar superconducting transition, although the exact position and nature of the transition depends upon the thickness and purity of the film. The electrodeposited film does show a transition from metallic to superconducting behaviour at approximately 4.5K in a 100 Gauss field (Fig 5). The magnitude of the transition, when correlated to the charge passed during synthesis, further indicates that the titanium nitride film is the major product of reaction. The position of the critical temperature, towards the upper end of the temperature range found for titanium nitride, indicates that as well as being relatively pure, the layer is also of relatively high crystallinity.

Experiments have also been performed using liquid ammonia/potassium amide electrolyte at ambient temperature and at a pressure of 10 atmospheres. Under these conditions both films and particles of titanium nitride can be produced. Energy dispersive x-ray spectroscopy (EDX) studies show the presence of nitrogen and titanium in thin film produced by this method, and significantly show no sign of oxygen incorporation into the film. The Raman spectra (Fig 6) of both film and particles produced at high current densities and at room temperature/10 atmospheres are very similar to the spectrum obtained from a commercial sample of titanium nitride. Powder X-ray diffraction of either film or particles produced by this method shows only a broad background, indicative of either amorphous or nano-crystalline material. Electron diffraction of the particles using transmission electron microscopy (Fig 7) gives rise to a scattering pattern indicative of nano-crystalline material from which d-spacings of $2.47 \pm 0.02 \text{ \AA}$, $2.12 \pm 0.02 \text{ \AA}$, $1.52 \pm 0.02 \text{ \AA}$, $1.28 \pm 0.01 \text{ \AA}$ have been obtained. These are entirely consistent with the observed d-spacings of the cubic phase of titanium nitride of 2.46 \AA , 2.12 \AA , 1.50 \AA and 1.28 \AA .

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In order to determine whether the method as applied to titanium was applicable to other metals, the technique was also used to produce films on molybdenum. Fig 8 shows CVs for the oxidation of a molybdenum electrode which had been pretreated in an analogous manner to titanium in order to remove its surface oxide. As with titanium, it is clear that oxidation of the molybdenum electrode results in the progressive shift of the oxidation to higher potentials, which shows that the deposited film is relatively inert. The relatively high pseudo-capacitance also demonstrates that the film is relatively conducting. Chronoamperometric studies (Fig. 9) produce current time transients of similar form to titanium, which is further evidence for the formation of a surface nitride film. As with titanium, heating the solution resulted in an increase in current, as did increasing the applied voltage. Also as with titanium, at increased current and elevated temperatures, particles are produced rather than a surface film. As further evidence for general applicability, particles are also formed in the oxidation of pretreated tungsten under analogous conditions. Nitrogen gas could not be detected in any of these reactions as a product.

In conclusion, these experiments have demonstrated that electrochemical oxidation of an electrode in liquid ammonia, with an amide salt as background electrolyte, results in the deposition of nitride. The thickness of the layer can easily be controlled by control of the oxidation charge, and it is thus possible to create layers ranging in thickness from one atomic thickness to thousands of atomic thicknesses, according to need. The rate of deposition can be controlled by changing the electrode potential and/or the temperature. Variation of the oxidation current, by varying the rate of deposition, will also vary the morphology of the film; for example a lower current passed for longer times will tend to produce a more controlled growth and more consistent morphology. By using pressurised vessels or supercritical ammonia, synthesis at or near room temperature is possible.

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CV studies indicate that reduction of the deposited nitride layer occurs at potentials at or below 0V, and results in an increased pseudocapacitance. It seems likely that the titanium species in the film is being reduced and
5 changing the film stoichiometry and hence its conductivity. This may well prove an important method of changing the film stoichiometry by changing the oxidation states of the film species and hence tailoring the electronic properties of these thin films.

10 The methods of the invention have several major advantages over existing techniques for the fabrication of thin nitrogen-containing films. These include:

- the in situ removal of protective oxide layers
- the use of amide electrolyte to preclude the
15 incorporation of contaminants and to favour the formation of nitrides over amido species
- the electrochemical control of deposition rate and morphology
- the formation of films at low temperature, allowing the
20 coating of thermally sensitive substrates and the formation of thermally unstable nitrides
- the control of film stoichiometry and redox composition
- the coating of substrates of irregular shape.

Electrochemical oxidation methods according to the
25 invention will enable the electrochemical synthesis of a wide variety of thin film and powder nitrides by oxidation of the appropriate metal or semiconductor. The nitrides thus produced will find uses in many different fields, for example in semiconductor manufacture, as wear resistant
30 coatings, as tap and die cutting surfaces, as machine cutting surfaces, in optical and electro-optical device fabrication, in the production of conductive interconnectors for integrated circuits, as anti-reflection coatings, in fuel cell manufacture and battery manufacture, as protective
35 coatings for nuclear cannisters and for conferring chemical corrosion resistance to components, as protective coatings

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for jewellery, as catalysts, and to provide colour effects on metal surfaces.

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CLAIMS

1. A method of producing a nitride film or powder by electrochemical oxidation of a substrate comprising an electrically conductive substance in an electrolyte
5 comprising an amide salt in liquid or supercritical ammonia.
2. A method according to claim 1, wherein the substrate substance and the operating conditions are chosen so that the free energy of formation of the nitride at the operating temperature and pressure is negative.
- 10 3. A method according to claim 1 or claim 2, wherein the substrate comprises a transition metal, a p-block metal or a semiconductor or any alloy or mixture thereof.
4. A method according to claim 3, wherein the substrate comprises one or more of: titanium, zirconium,
15 hafnium, vanadium, niobium, tantalum, chromium, molybdenum, tungsten, manganese, iron, steel, cobalt, nickel, rhenium, aluminium, gallium, indium, silicon, germanium, an actinide, a lanthanide, gallium arsenide and indium phosphide.
5. A method according to any preceding claim, wherein
20 the substrate is doped.
6. A method according to any preceding claim, wherein the electrically conductive substance is provided as a layer on a base substrate.
7. A method according to any preceding claim, wherein
25 the electrolyte comprises potassium amide, sodium amide, lithium amide, rubidium amide or caesium amide.
8. A method according to any preceding claim, carried out at atmospheric pressure at a temperature in the range -78°C to -33°C.

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9. A method according to any of claims 1 to 7, carried out at ambient temperatures and at a pressure of between 1 and 10 atmospheres (1.013×10^5 to 1.013×10^6 N.m⁻²).
- 5 10. A method according to any preceding claim, wherein, prior to the electrochemical oxidation, the electrically conductive substrate is subjected to electrochemical reduction to remove any surface oxide layer.
11. A method according to any preceding claim, for 10 producing titanium nitride film.
12. A method according to any preceding claim, for the manufacture of semiconductor compounds, wear resistant coatings, tap and die cutting surfaces, machine tool cutting surfaces, electro-optical and optical device compounds, 15 conductive interconnectors for integrated circuits, anti-reflection coatings, fuel cell components, battery components, nozzles, protective coatings for nuclear canisters, protective coatings for conferring chemical corrosion resistance to components, protective coatings for 20 jewellery, catalysts and for producing colour effects on metal surfaces.
13. A process according to any of claims 1 to 10 for the production of a nano-crystalline powder.
14. A process according to claim 13, wherein the 25 nano-crystalline powder is suitable for use in low temperature sintered components, catalysis, colloids, rheology, and molecular scale electronic devices.
15. A nitride film or powder produced by a method according to any preceding claim.

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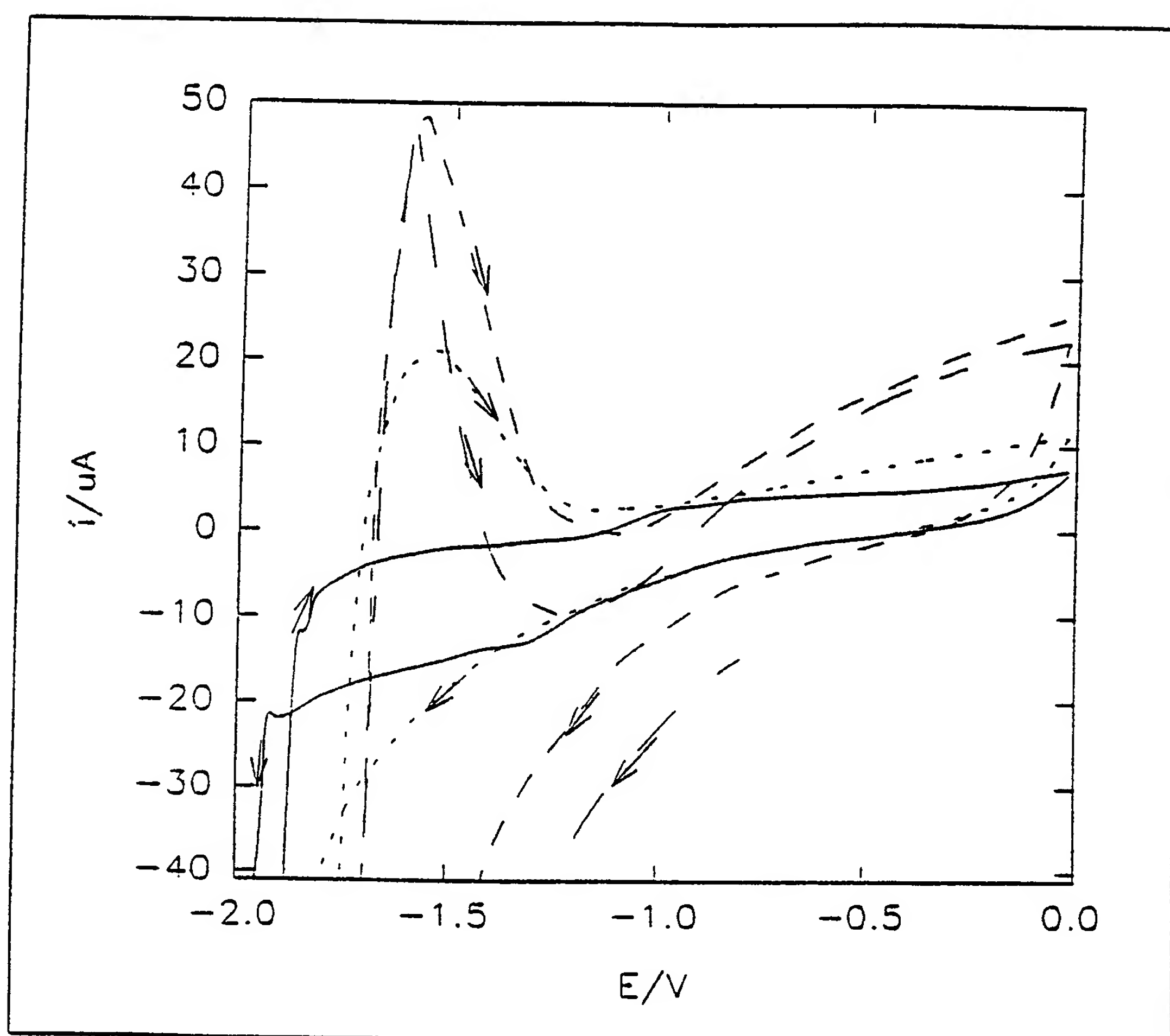


FIG 1

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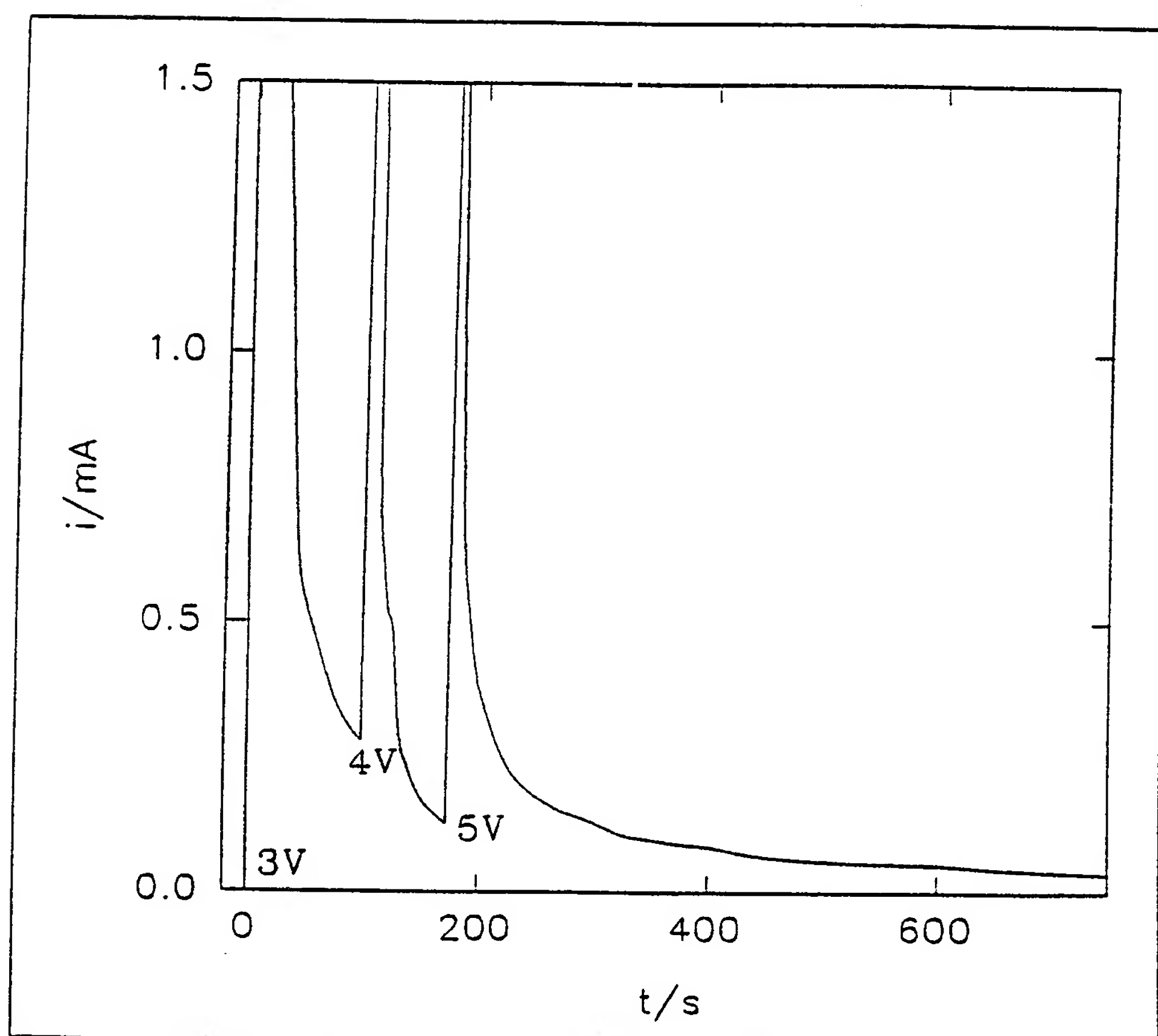


FIG 2

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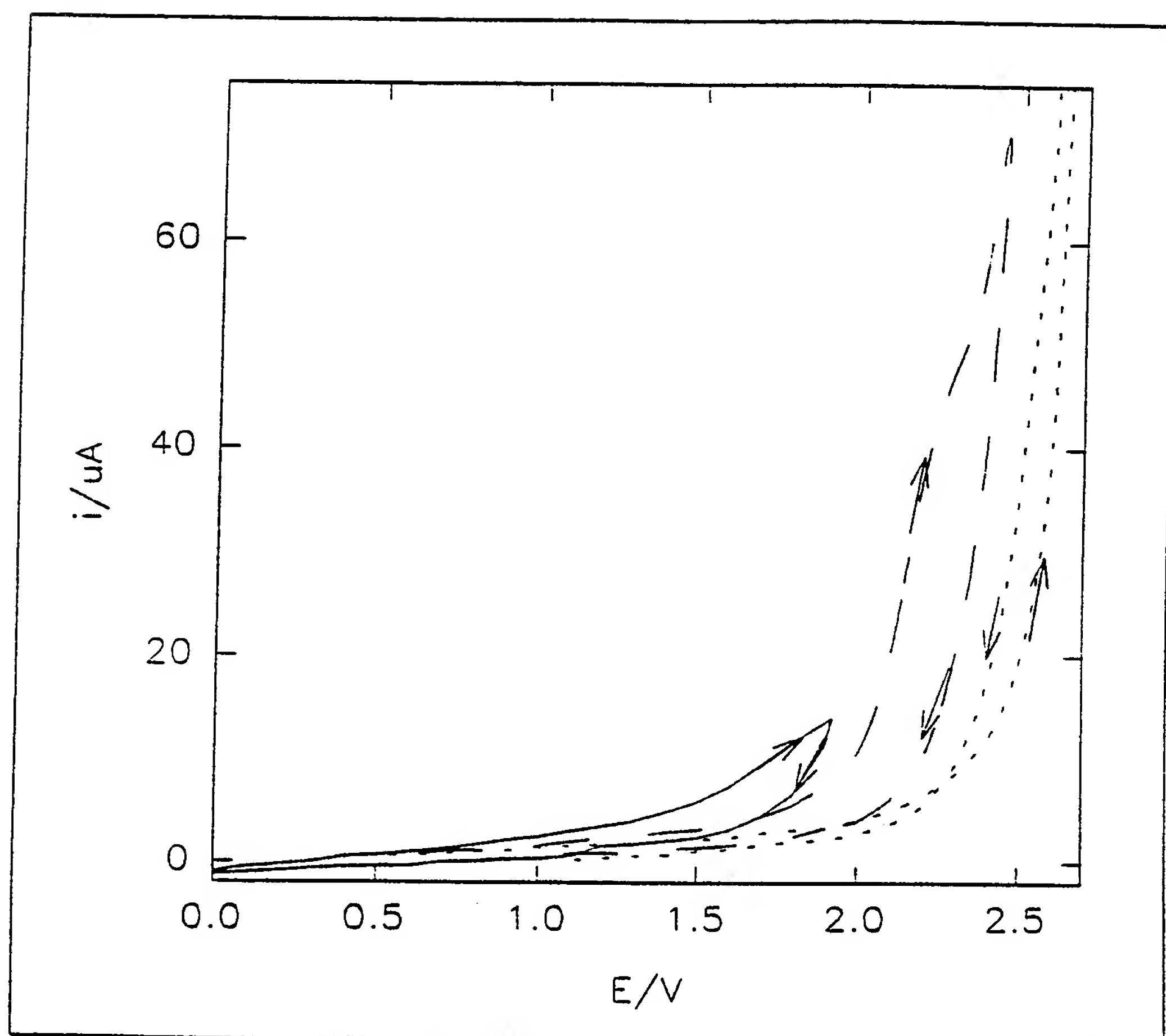


FIG 3

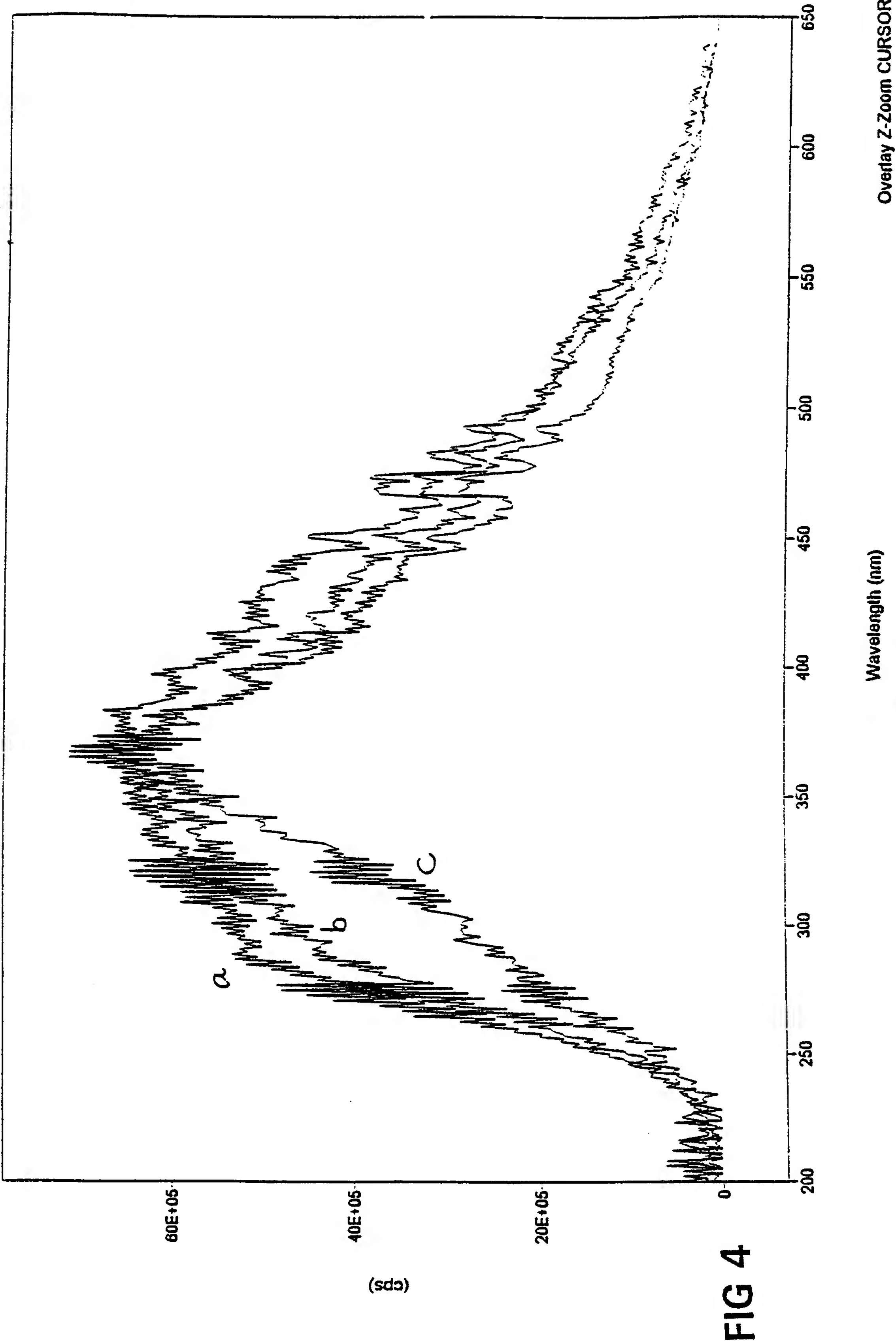
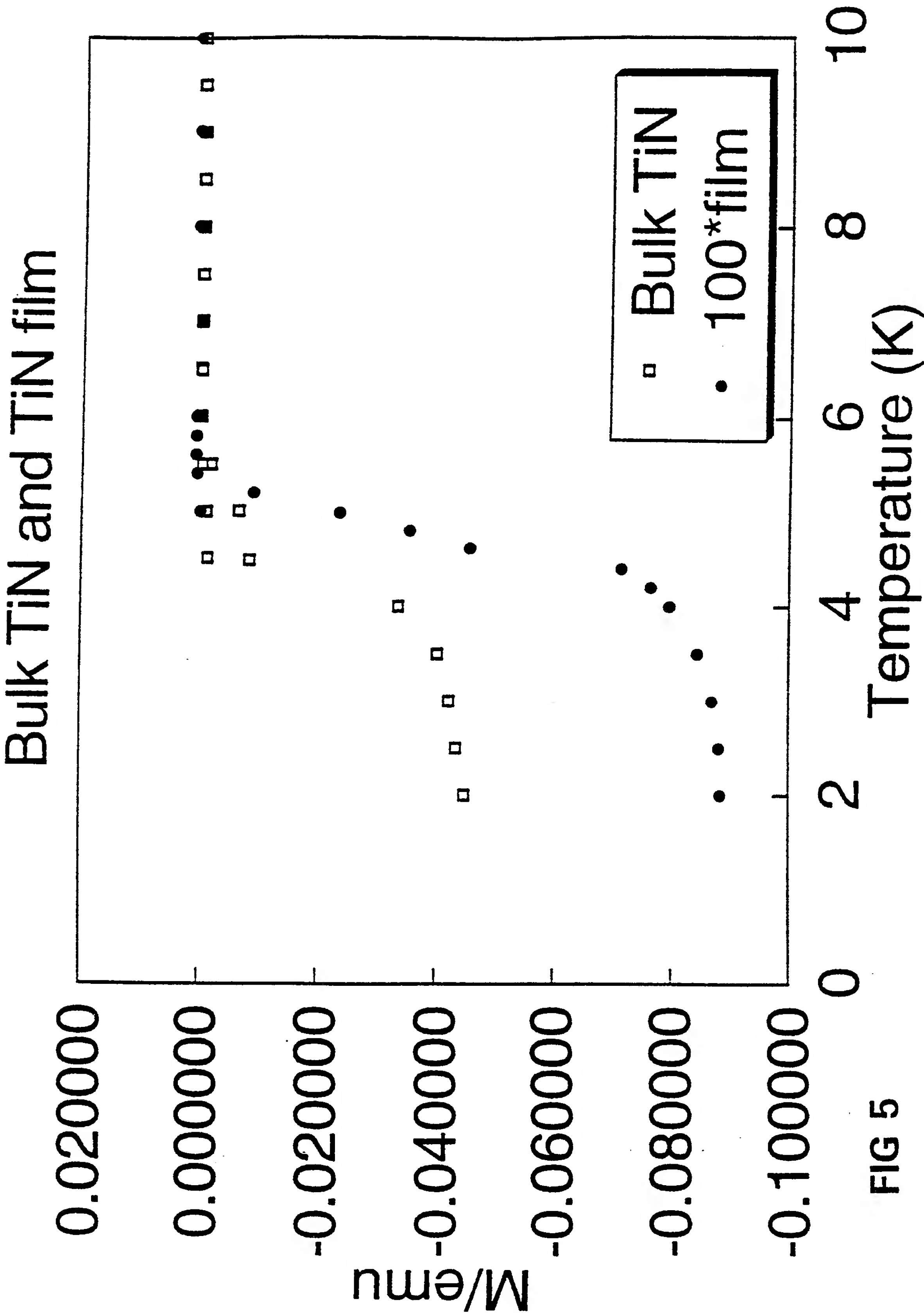


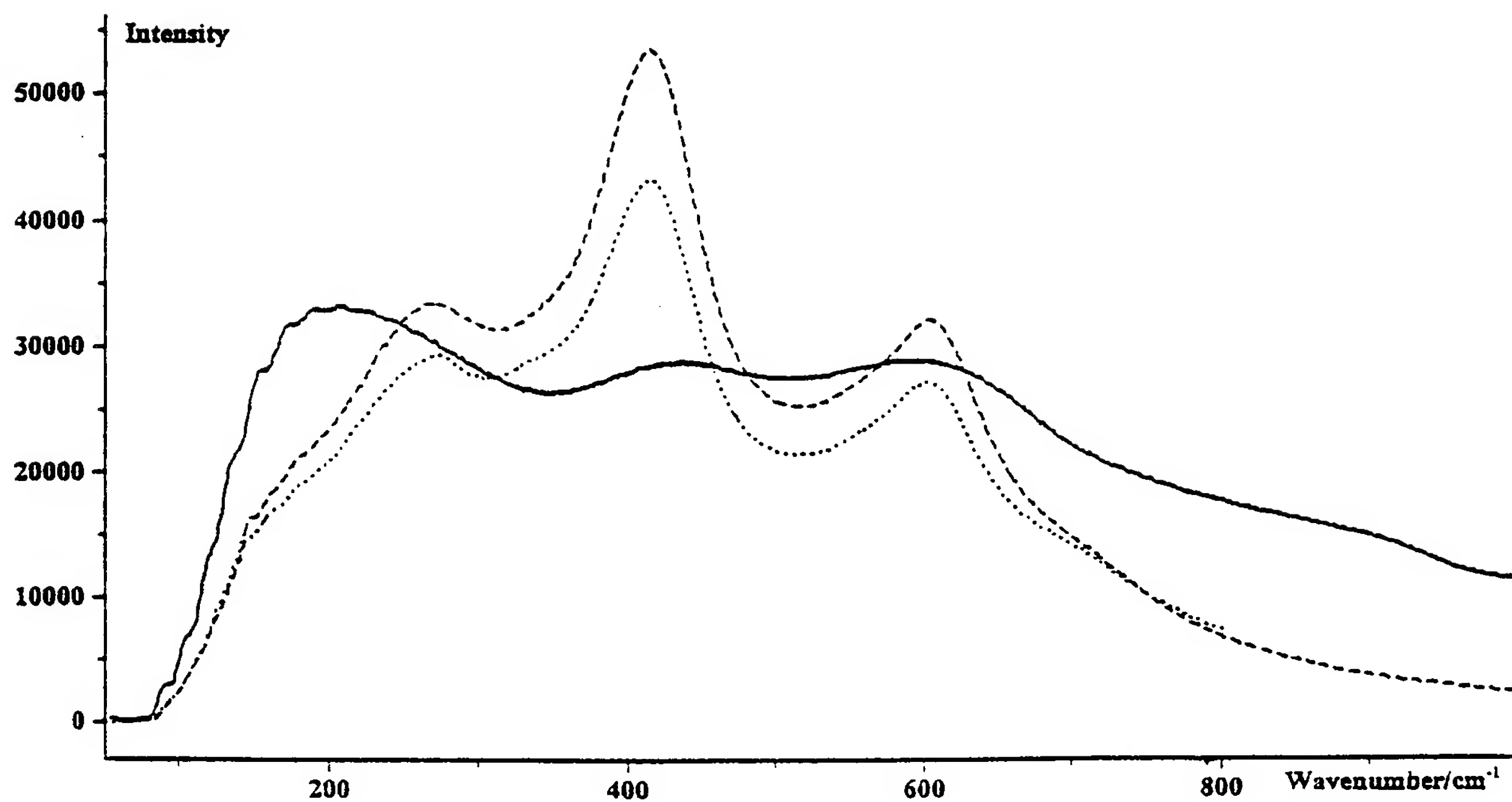
FIG 4

File # 2 = COLIN11

Synchronous Scan on tin thin film 2 slits 2nm



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Raman spectra of (- - -) commercial TiN powder, (. . . .) electrochemically synthesised TiN powder (—) electrochemically synthesised TiN film.

FIG 6

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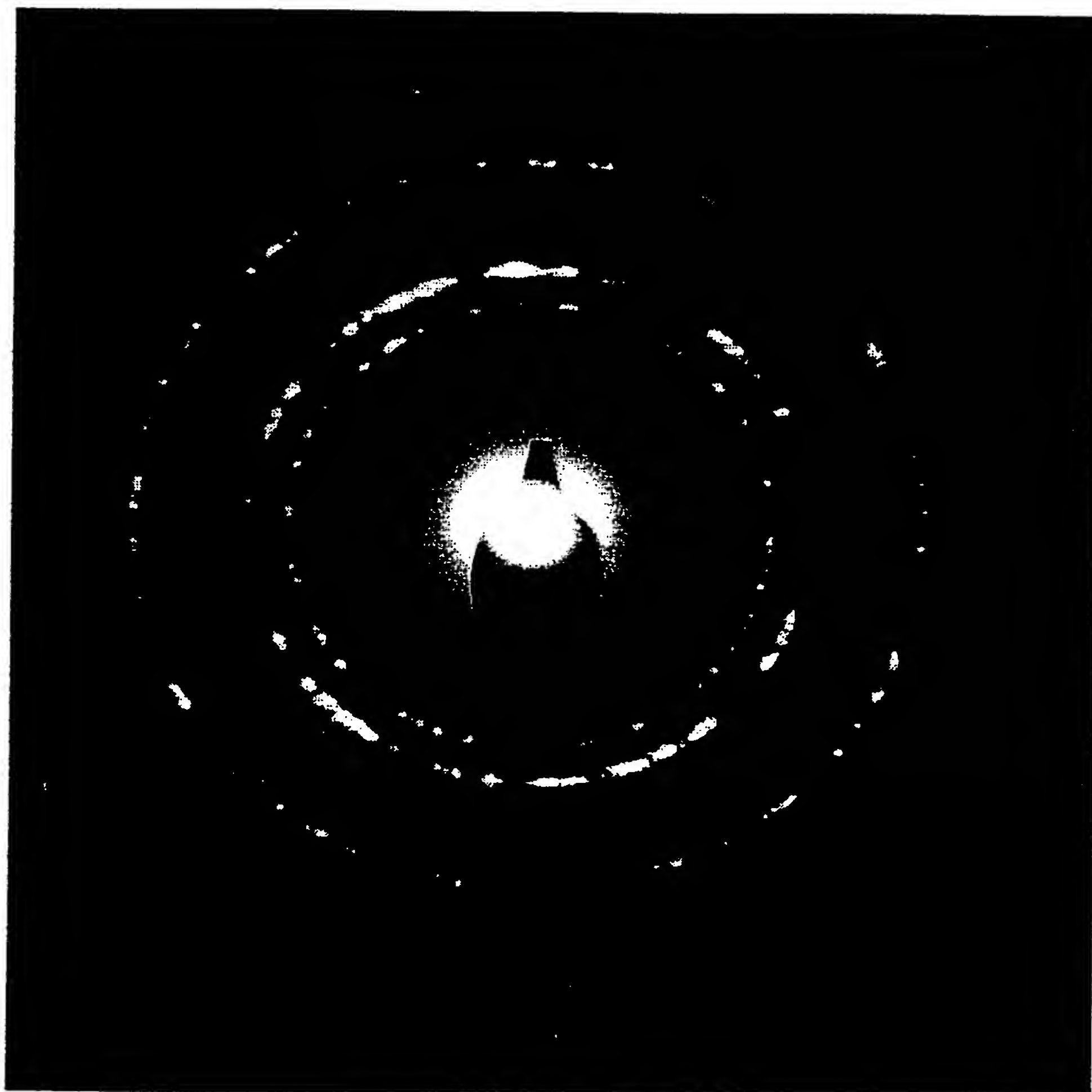


FIG 7

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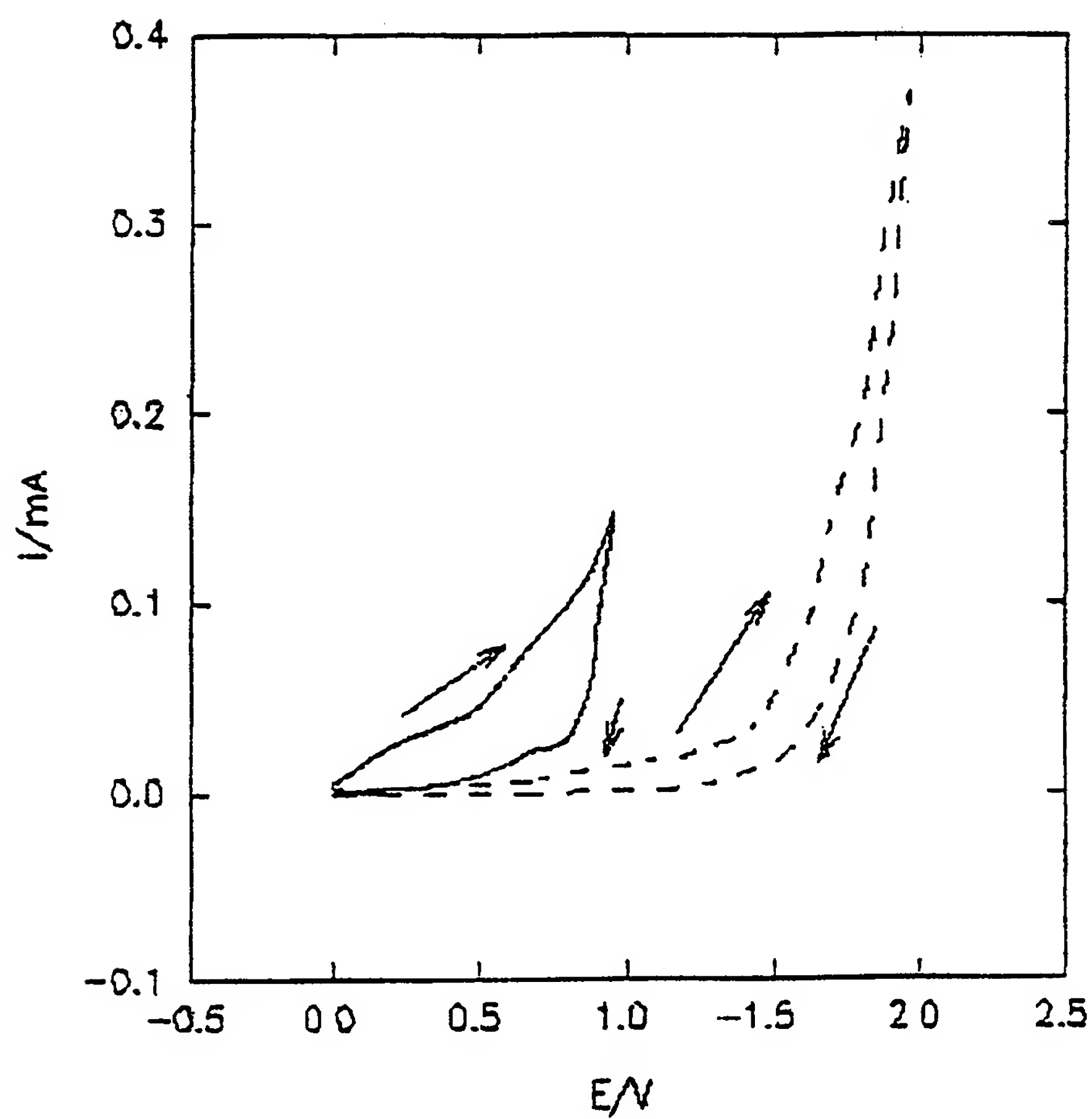


FIG 8

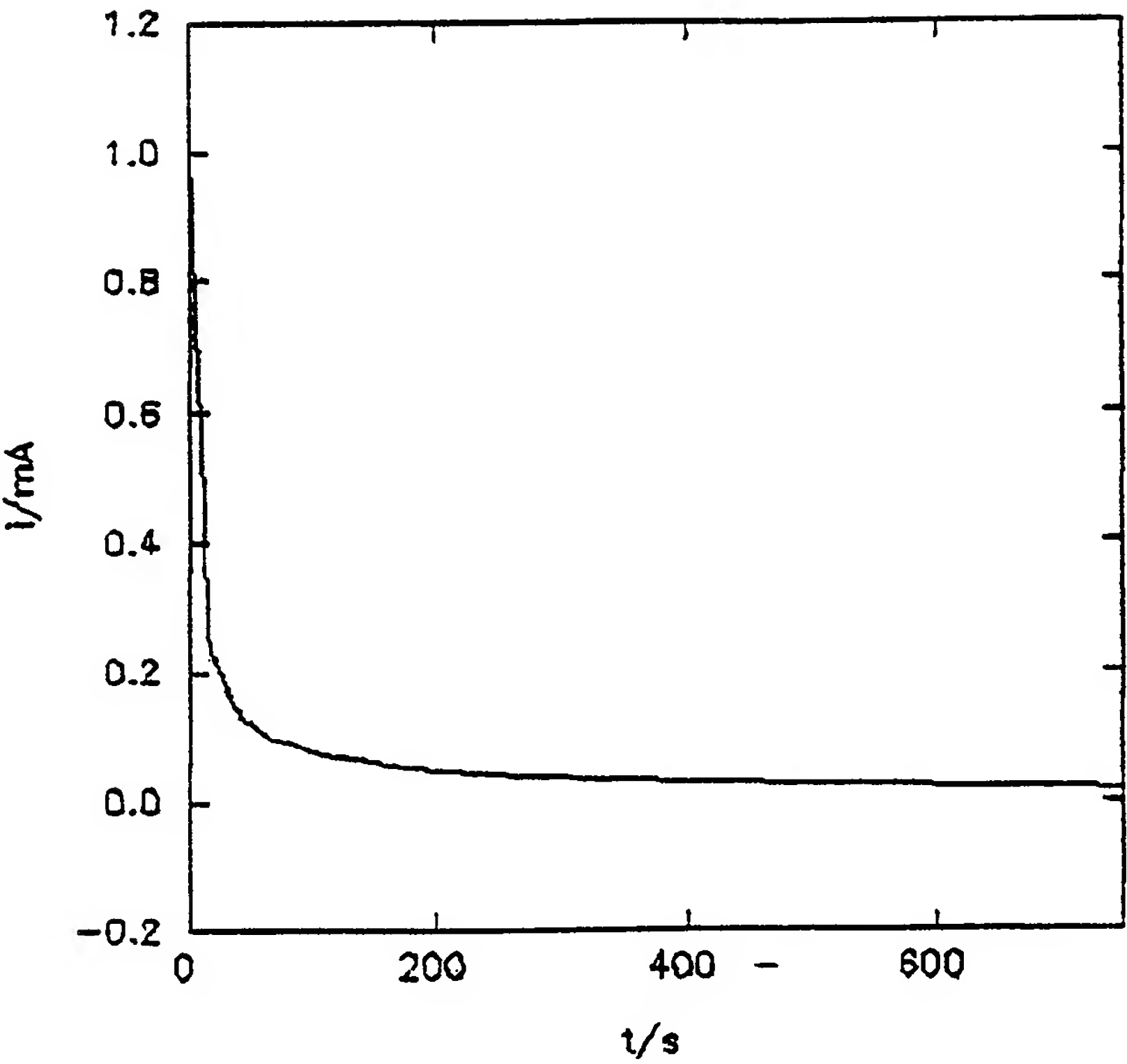


FIG 9